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P-type microcrystalline silicon films prepared by VHF-PECVD technique

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Abstract : Very High Frequency Plasma Enhanced Chemical Vapour Deposition Technique (VHF-PECVD) is very much important for growth of microcrystalline silicon material at high deposition rate. In this work, p-type μc-Si:H films have been developed by VHF-PECVD technique at low substrate temperature (250°C) and low power (55 mW/cm^2). The effect of plasma frequency on optoelectronic and structural properties have been studied. The size of crystallites developed in silicon matrix varies from 100 Å to 500 Å and the optical bandgap is 1.86 eV. The maximum conductivity of 35.7 Scm^{-1} has been achieved with a high deposition rate (33.00 Å/min) at 63.75 MHz plasma excitation frequency.

Keywords : VHF-PECVD, X-ray diffraction, TEM, Raman spectra

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1. Introduction

p-type microcrystalline silicon (μc-Si:H) layer having high conductivity and transparency can effectively replace the doped amorphous window layers (a-Si:H, a-SiC:H) of the p-i-n solar cells, to increase built-in-potential and decrease series resistance. Microcrystalline film grows under an equilibrium condition between deposition and etching. Usually high hydrogen dilution is used to prepare μc-Si:H by PECVD or other CVD techniques but the deposition rates are very low (5-10 Å/min). It has been observed that the improvement in crystallinity suppress the growth rate [1] and increase in the deposition temperature improves the grain size [2]. However, high temperature is not suitable in a-Si technology and large area electronics.

In usual PECVD technique 13.56 MHz frequency is used to excite the plasma. Now the very high frequency (VHF) PECVD technique becomes very much important for the growth of μc-Si:H, leading to high quality material at lower plasma excitation power and deposition temperature [3, 4]. It is reported from plasma diagnostics [5, 6] and impedance analysis [7] that a higher density and less energetic ion flux and a higher atomic hydrogen and radicals flux to the growth surface lead to favorable growth under VHF conditions. The details of the plasma studies and impedance analysis are also reported [8, 9].

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2. Experimental details

The samples were prepared in a capacitively coupled multichamber PECVD system (Glasstech Solar Inc., USA) with plasma excitation frequencies between 13.56 to 120 MHz. Semiconductor grade source gases (Matheson Inc., USA) *e.g.* silane (SiH_4), methane (CH_4), diborane (B_2H_6; 1 % in hydrogen) and hydrogen (H_2) were used. For plasma excitation, a broad band generator (0-200 MHz) and a network matchbox with a stepwise variable inductance are used. The optimum matching is achieved by minimizing the reflected power at a given frequency and then further adjusting the frequency to decrease the reflected power.

The samples were deposited from SiH_4 highly diluted in H_2 at 55 mW/cm^2 power density. The doping concentration [$X_B = B_2H_6/(SiH_4 + B_2H_6 + H_2)$] and substrate temperature were fixed at 4.97×10^{-5} and 250°C respectively. The samples were deposited at various plasma excitation frequencies (ν_{ex}) between rf (13.56) to VHF range at a sufficiently low pressure of 0.3 Torr.

Substrates used were 7059 corning glass for optoelectronic measurement and carbon coated copper grid for transmission electron microscopy. The thickness of the films were measured by a Stylus type instrument (Planer product, UK). Dark and photoconductivity measurements were carried out in a gap cell configuration after annealing the sample in vacuum (~ 10^{-6}) at 150°C for about an hour. The photoconductivity was measured under white light intensity of 60 mW/cm^2 using a tungsten halogen lamp. The optical absorption spectra was measured by

Hitachi 330 double beam spectrophotometer. The bonding configuration was investigated by Fourier Transform Infrared Spectrophotometer (Perkin Elmer). For structural study, Transmission Electron Microscopy (TEM), Raman Study and X-ray Diffractometry (XRD) have been carried out. The effect of frequency (RF-VHF MHz) on the film properties have been investigated.

3. Results and discussions

3.1 Optoelectronic properties :

The optical absorption spectra in the UV-VIS range of p-type μc-Si:H films prepared at different frequencies are shown in Figure 1 and Figure 2 shows the corresponding deposition rate. The increase of frequency causes no significant variation of the absorption spectra. The deposition rate (R_d) increases monotonically from 11.7 Å/min to 36.7 Å/min as the frequency increases from rf (13.56) to 79 MHz. The R_d drops again to 23.3 Å/min with further increase of ν_{ex} to 95.7 MHz.

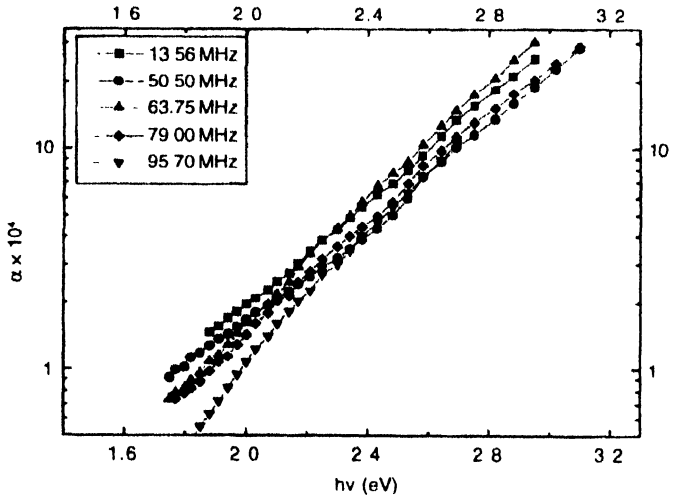

Figure 1. Optical absorption coefficient (α) of μc-Si:H films deposited at different frequencies

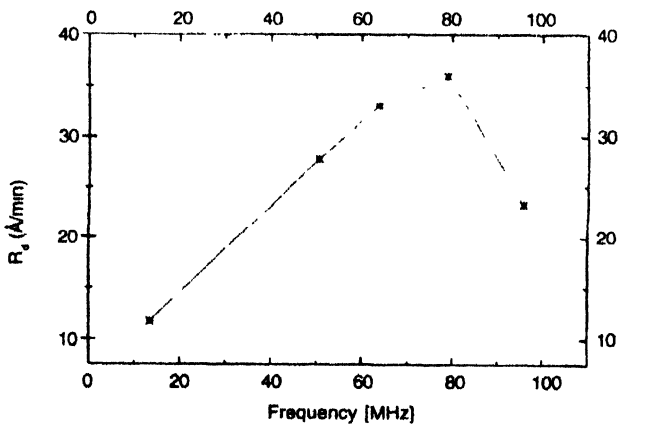

Figure 2. Variation of deposition rate at different excitation frequencies.

The dark conductivity (σ_d) and its activation energy (E_a) as a function of excitation frequency are plotted in Figure 3. The dark conductivity increases monotonically from 0.51 Scm^{-1} to 35.7 Scm^{-1} along with decrease of activation energy from 68.8 meV to 15.8 meV with the increase of frequency from rf (13.56 MHz) to 63.75 MHz.

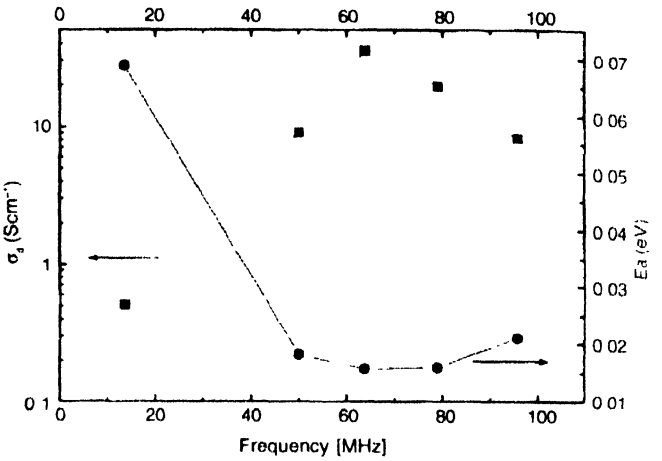

Figure 3. Variation of dark conductivity and activation energy of p-type μc-Si:H with frequency

The μc-Si:H growth process is a balance of deposition and etching mechanism which is known as partial chemical equilibrium (PCE) [10]. This can be achieved by lowering of silane concentration in hydrogen or increasing the discharge power in case of rf-PECVD technique. The significantly low deposition rate < 12 Å/min have been obtained even at sufficiently high power of 150 mW/cm^2 at 13.56 MHz [11]. In rf PECVD at low deposition temperature ($\lesssim$ 200°C), grains do not coalesce and do not reconstruct at the grain boundaries to form larger grains ; whereas, in case of VHF-Glow discharge technique the energy released by the reactions occurring at the film growth surface may raise locally the temperature of a few atomic layers at the growing surface [12]and favours chemical annealing [13]. Prasad *et al* [3] reported higher power transfer efficiency, lower plasma potential and lower sheath potential at high frequency compared to rf frequency. The higher power transfer efficiency at high frequency enhance dissociation of the reactant gases [14] even at low discharge powers. The increased radical density (hydrogen and advantageous SiH_x precursors) traverse the sheath with smaller loss [7] to reach the surface of the growing film which provide both an selective erosion of unfavourable bonds such as hydrogen or weakly bonded silicon atoms and favours fast growth of crystalline grains. As a result, deposition rate increases continuously with increase of excitation frequency (ν_{ex}) upto 79 MHz. The maximum deposition rate at 70 MHz has been reported by others [15, 16]. The growth mechanism of crystalline silicon at low temperature, can be explained by a model proposed by Keppner *et al* [17]. The two necessary conditions for the model are as follows : (i) high surface mobility is essential so that radicals can stick at crystal site and (ii) the energy of impinging particle on the growth zone must not exceed the threshold energy of defect formation. The advantage of plasma processes is that the dissociation of silane occurs due to electron impact where the substrate temperature can be kept

at a low value. Keppner *et al.* [17] reported that for formation of c-Si lattice by rf-PECVD process, ion energies higher than the threshold energy (E_{th}) of defect formation are required; whereas, in case of VHF-GD technique ion energies lower than E_{th} have been estimated. So VHF-GD technique favours better crystalline structure. An improvement in crystallinity inspite of a high deposition rate is a characteristics of both n-, intrinsic and p-type microcrystalline films [18-20]. For our high frequency samples, the better crystallinity provides enhanced doping efficiency and hence higher conductivity and lower activation energy have been observed in p-type μc-Si:H compared to p-type a-Si:H. The highest conductivity of 35.7 Scm $^{-1}$ has been achieved at 63.75 MHz. The further increase in frequency (79 & 95.7 MHz), leads to structural deterioration of the crystallinity, as a result, conductivity decreases. An optimum frequency of deposition also have been reported by others in the study of microcrystalline growth [21, 22]. The activation energy shows the reverse replica of σ_D, an increase of dark conductivity is accompanied by the shift of Fermi level (E_F) more towards the valance band. Prasad [23] has reported a conductivity of 30 Scm^{-1} at a substrate temperature of 160°C but with higher power density (75 mW/cm^2) by VHF-PECVD technique. Heintze *et al* [24] also reported a conductivity of 39 Scm^{-1} at 75 mW/cm^2 at 200°C substrate temperature. But in our case, the power density is much lower (55 mW/cm^2) without significant loss in conductivity (35.7 Scm $^{-1}$). The increase of frequency increases the deposition rate due to formation of more SiH precursors [25] and in this case it becomes maximum at 79 MHz with a deposition rate of 36.7 Å/min.

3.2 Structural studies :

The transmission electron microscope image (TEM) and the diffraction pattern (TED) for the films prepared at 63.75 and 95.7 MHz have been shown in Figure 4 (a-d). The particles size varies from 100 Å to 500 Å and 40 Å to 160 Å at 63.75 and 95.7 MHz respectively. The films at 63.75 MHz shows two bright rings corresponding to <220> and <311> planes of c-Si; whereas, film at 95.7 MHz exhibits <220>, <311>, <400>, <331>, <422>, <511> and <400> planes. In order to understand the effect of frequency on conductivity, further structural characterizations are necessary. Figure 5 shows typical X-ray diffraction pattern of the above two films using CuKα radiation. Clearly, <220> peak of c-Si is observed at 63.75 MHz, whereas film at 95.7 MHz shows no significant peak due to its small grain size. At 63.75 MHz, a preferential growth of crystallites in the <220> direction results larger grain ~ 500 Å. On the otherhand, at 95.7 MHz small crystallites are formed due to crystallites growth in different directions. As a result, former shows higher conductivity. Prasad [23] reported maximum crystalline size of 320 Å with conductivity of 20 Scm^{-1} prepared at a much higher rf power (150 mW/cm^2). But in this case, larger grains have been formed (500 Å) resulting higher conductivity (35.7 Scm^{-1}) as a much lower power (55 mW/cm^2).

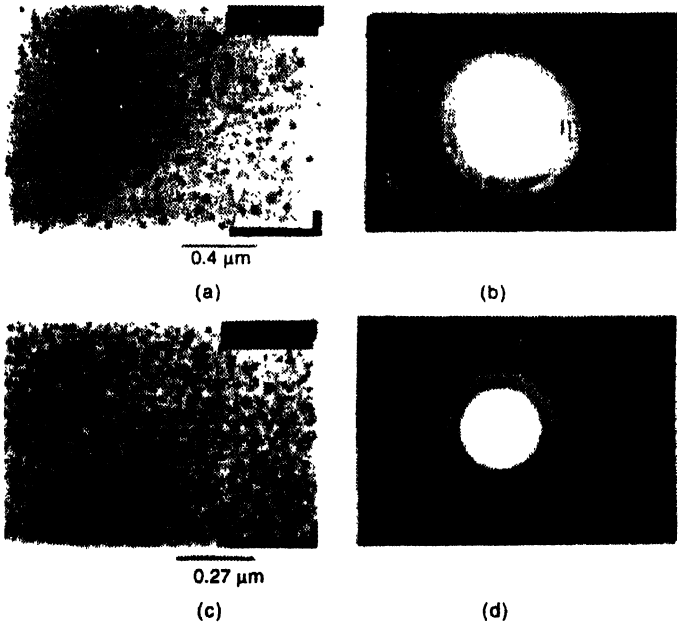

Figure 4. Transmission electron micrograph and its diffraction pattern for the μc-Si:H films prepared at 63.75 MHz (a & b) and 95.7 MHz (c & d).

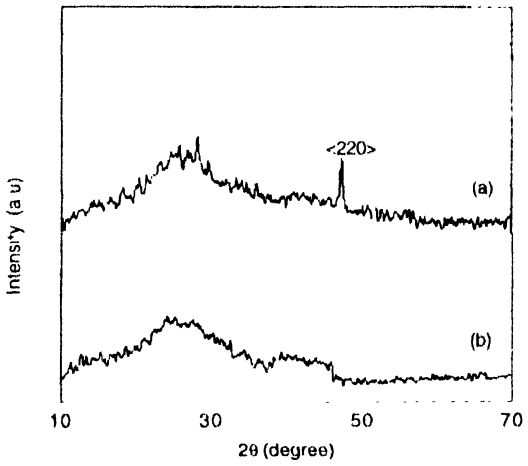

Figure 5. X-ray diffraction pattern of p type μc-Si:H films prepared at (a) 63.75 MHz and (b) 95.7 MHz

To get more information about the structure of the amorphous microcrystalline mixed phase material, Raman spectra of two samples prepared at two different frequencies, 63.75 MHz and 95.7 MHz respectively are shown in Figures 6 (a, b). Each Raman spectra may be deconvoluted into three separate peaks, (i) the crystalline component peak at 520 cm^{-1}, (ii) amorphous component peak at 480 cm $^{-1}$ and (iii) an intermediate component peak at 494-507 cm^{-1} which is associated with bond dilution at grain boundaries [26]. The crystalline volume fraction X_c is estimated from

$$X_c = \frac{I_c + I_{gb}}{I_c + I_{gb} + yI_a}$$

where I_c, I_a and I_{gb} are integrated intensity of the crystalline, amorphous and intermediate peaks respectively. Y is the ratio of

the cross section for the amorphous to crystalline phase, which varies with the grain size. The crystalline volume fraction are 83.5% and 64.5% [for simplicity using y = 1] at 63.75 MHz and 95.7 MHz respectively. This results also confirm the formation of better crystallinity at 63.75 MHz in comparison to 95.7 MHz frequency.

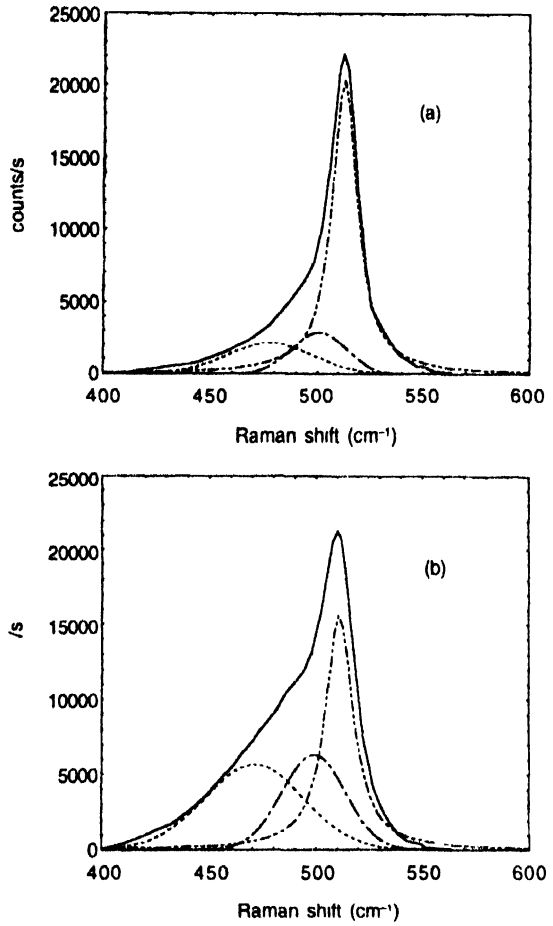

Figure 6. Raman spectra of μc-Si:H films prepared at (a) 63.75 MHz and (b) 95.7 MHz plasma excitation frequency.

4. Conclusions

p-type μc-Si:H films have been developed by VHF-PECVD technique at low substrate temperature (250°C) and low power (55 mW/cm^2). An optimum frequency of 63.75 MHz has been observed with results in the maximum conductivity of 35.7 Scm^{-1} with a high deposition rate (33.00 Å/min). The film shows 83.5 %, crystalline volume fraction with quite large grain size of 500 Å due to preferential growth in the <220> direction. However, deposition rate reaches its maximum value of 36 Å/min at 79 MHz.

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